EFFECTS OF DIFFERENT MODES OF COAGULATION AS PRETREATMENT TO MEMBRANE FILTRATION FOR DRINKING WATER PRODUCTION IN SMALL SYSTEMS

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INTRODUCTION

Study Objectives

In the United States, over 246 million people are served by 58,908 community water systems. Approximately eighty six percent of these systems are termed small or very small systems. Small water systems are those that serve fewer than 3,300 people and very small water systems serve fewer than 500 people. These facilities are the most frequent violators of federal regulations. Their most common infringements are microbial violations and failure to report and monitor. To bring these systems into compliance will require technologies, operator abilities, financial resources, and institutional arrangements.

The use of membrane technologies for aqueous separations has become very popular over the past twenty years. Successful use of membranes was first seen with desalination of brackish water and seawater. However, improvements in materials and manufacturing technology, mechanical configuration, and cleaning, have expanded membrane technology to the treatment of waters of varying quality. Communities are searching for alternatives to conventional treatment for the production of high quality effluents for various applications and are looking to membrane technologies as they become more popular.

Membrane filtration offers small systems a high efficiency, easy-to-operate alternative to improve the finished water quality and the biological stability of the finished water. However, the economic use of membrane filtration in small systems is often hindered by fouling, which increases applied pressure drops and cleaning

frequencies, and the associated decrease in removal efficiency as the pressure drop increases.

There are two major types of fouling: abiotic fouling and biofouling. Abiotic fouling is often associated with accumulation of substances, mainly clays and natural organic matter (i.e., humic acid) on the membrane surface or within the membrane pore structure [1-2]. Biofouling is caused by the accumulation of microorganisms onto the membrane. These microorganisms accumulate and grow on the membrane due to high concentrations of low molecular weight organic carbon compounds such as acetate and amino acids that serve as nutrient source for bacteria present in the influent water.

Currently, the most common method to prevent fouling is by pretreating the influent to the membrane process with the application of chemicals. However, chemical additions require caution since several chemicals are incompatible for long-term use, may cause bacteria to become more resistant, and may add impurities to the treated effluent [3-4].

Ordinary coagulation, as a pretreatment process, can substantially reduce the concentration of biodegradable organic matter found in raw water; thus, it can decrease the potential for fouling and enhance membrane rejection. Organic removal depends on the water matrix characteristics and the settling conditions (coagulant type and doses, coagulation conditions, settling type, etc). Biodegradable dissolved organic carbon (BDOC) removals of 66-76% in warm water (>18^{o}C) and 50% in cold water were reported at the St. Rose treatment plant in Montreal, Canada [5]. Joret et al. (1989) reported BDOC removals of approximately 50% by coagulation [6].

Related studies have shown that there was no significant difference in the removal rate of UV-254 by ordinary versus in-line coagulation modes, both achieved removal rates over 30% [7]. Further, this study determined coagulant precoating of membranes was more efficient than ordinary and in-line coagulation modes, used lower quantities of coagulant, and consumed less coagulant. Thus, the removal efficiency of the membrane process was increased.

The objective of this study was to find a method of coagulant pretreatment to preceed membrane filtration that would be both effective and cost efficient for small water systems. In order to achieve this objective, the following tasks were performed:

The objective of task 1 was to characterize ultrafiltration, nanofiltration, reverse osmosis, and low pressure reverse osmosis membranes using bench scale filtration experiments. The commercial membranes characterized were:

CQ – Ultrafiltration (GE Water – "Osmonics")

NTR7450 – Nanofiltration (Hydranautics)

CK – Reverse Osmosis (GE Water – "Osmonics")

ESPA – Low Pressure Reverse Osmosis (Hydranautics)

To do this characterization step, two different raw waters were used, a laboratory designed raw water that contained organics, inorganics, and bacteria and water collected from Lake Erie. The membranes were characterized with regards to: specific flux decline, turbidity, total dissolved solids (TDS), conductivity, hardness, UV 254, dissolved organic carbon (DOC), and bacteria growth.

The objective of the second task was to determine which coagulant and concentration would be most effective in future testing by utilizing jar testing. The two

coagulants tested were 2% ferric chloride and 2 % ferrous chloride in concentrations of 0, 25, 50, 75, and 100 mg/L. These coagulants were chosen, because ferrous and ferric allow for arsenic co-precipitation through Fenton's reaction. Each coagulant and concentration was characterized with regards to turbidity, pH, TDS, conductivity, and UV 254. After determining that 2% ferric chloride in a range of 0-25 mg/L was the most effective, another test with concentrations of 0, 5, 10, 15, 20, and 25 mg/L was done.

Task 3 combined CQ and the 25 mg/L 2% ferric chloride in four different bench scale filtration set ups. The first set up reflected a traditional coagulation and settling process. The second set up was a coagulation slurry, where 10 ml of a coagulant slurry was placed directly on the membrane before water was passed through it. The third setup formed a dynamic membrane layer by passing 10g of ferric chloride in 1000 mL of DI water across the membrane before the raw water was tested. The last set up was an inline set up, where the coagulant was added to the raw water flow before being passed across the membrane. These setups were characterized with regards to: specific flux decline, turbidity, TDS, conductivity, hardness, UV 254, DOC, and bacteria growth.

Background

Fouling represents the major constraint to more cost-effective, and therefore expanded, application of membrane technology in drinking water and wastewater treatment. Fouling can occur in several forms and can vary from high- to low-pressure membranes. Many researchers have suggested that the humic substances fraction of natural organic matter (NOM) is a major foulant that controls the rate and extent of membrane fouling [8-15]. However, recent studies have reported that hydrophilic (non-

humic) NOM could be the more dominant foulant. In the studies performed by Lin et al. [16] and Carroll et al. [17], residual dissolved NOM composed of small, neutral hydrophilic substances is strongly implicated in controlling the rate of fouling. Associated with wastewater treated to a secondary level is effluent organic matter (EfOM). EfOM consists of NOM contributed by the drinking water source plus soluble microbial products (SMPs) produced during biological treatment, and has relevance from the perspective of effluent-impacted drinking water sources or wastewater reclamation and reuse. Based on significant chemical differences, fouling potential varies according to the type of NOM [18].

The use of low-pressure membranes, microfiltration (MF) and ultrafiltration (UF), has increased dramatically over the last decade, in response to water regulations. In the mid-1990s, low-pressure membrane technology was most often employed in a direct filtration mode, with source water applied directly to the membrane. The practice has evolved and pretreatment in the form of chemical coagulation has now become more common and has led to the hybrid technology coagulation followed by ultrafiltration (C-UF). The progression from direct to integrated treatment (C-UF) has produced benefits in terms of membrane fouling reduction by solids while only minimal benefit relative to NOM fouling.

In crossflow processes, there occurs a formation of a secondary or dynamic membrane on top of the primary membrane. Dynamic membranes are formed by initially having colloids/particulates/NOM block the support pores. Once the pores are blocked, a transition time (45-120 minutes) is said to have elapsed and the formation of a cake filtration layer begins. Dynamic membranes were first reported in 1965 by workers at the

Oak Ridge Laboratories engaged in desalination research [19]. NOM forms cake layers that adversely affect membrane operation (i.e. irreversible fouling layers), while inorganic colloids have been observed to form desirable layers [20-21]. The presence of steady state layers of symmetric minerals of narrow particle size distribution on membranes have been associated with increased permeate volume, while the magnitude of the rejection increases with increasing the dynamic layer mass and irregularity [22]. This phenomenon is being exploited here by substituting the involuntary dynamic membrane with a layer of desirable properties.

METHODOLOGY

The methods and materials used for this study were adapted from and can be found in greater detail in Peng et al. 2004 and King et al. 2004 [8, 9, 23].

Membranes

For this study, four commercial water treatment membranes were examined. Below is a brief summary of operating and design information available for them.

CQ: Ultrafiltration membrane manufactured by GE Water – "Osmonics" has a cellulose acetate selective layer. Its functional groups are hydroxyl and acetate. Film thickness is approximately 3.3 mils. It has no formal charge. Using a DI water sessile drop, the contact angle was measured at about 55 degrees. Using several test liquids, a surface free energy was about 42 mJ/m^2. The pure water flux is about 300 gfd at an operating pressure of 50 psi. Recommended operating pressure is to operate at a flux to yield about 15 gfd. The recommended operating temperature is less than 86 ^oF. Recommended operating pH is between 5.0 and 6.5, but cleaning can be done at a pH between 3 and 8. This membrane is chlorine tolerant.

CK: Reverse osmosis membrane manufactured by GE Water – "Osmonics" has a cellulose acetate selective layer. Its functional groups are hydroxyl and acetate. Film thickness is approximately 3.3 mils. It has no formal charge. Using a DI water sessile drop, the contact angle was measured at about 55 degrees. Using several test liquids, a surface free energy was about 42 mJ/m^2. The pure water flux is about 300 gfd at an operating pressure of 50 psi. Typical operating flux is 10-20 gfd. Recommended operating pressure is between 60 and 200 psi. The

recommended operating temperature is less than 86°F. Recommended operating pH is between 5.0 and 6.5, but cleaning can be done at a pH between 3 and 8. This membrane is chlorine tolerant.

ESPA1: Reverse osmosis membrane manufactured by Hydranautics (San Diego, CA) has an aromatic polyamide selective layer. Its functional groups are carboxylic and amide. Film thickness is approximately 2000 angstrom. It is negatively charged and hydrophobic. Depending on the marker used, it has a molecular cut-off range between 100-300 Dalton. This membrane has an advancing contact angle of 58 and receding contact angle of 34 . The specific flux is 0.22 gfd/psi, with a recommended operating pressure of 75-150 psi. The operating temperature range is 0-45 C and pH range is 2-11. Since this membrane is a polyamide polymer, it has a limited chlorine tolerance.

NTR 7450: Nanofiltration membrane manufactured by Hydranautics (San Diego, CA) has a selective layer made from sulfonated polyether sulfone. It is negatively charged, hydrophobic, and has a molecular weight cut-off of approximately 500 Dalton. The contact angle for this membrane is 55° King et al. 2004. The specific flux is 0.33 gfd/psi, with a recommended operating pressure of 75-150 psi. The operating temperature range is 0-45 C and pH range is 2-11. This membrane can be exposed to chlorine concentrations around several hundred ppm.

Water Quality

The membranes were tested with two different raw waters during baseline testing; synthetic raw water and water collected from Lake Erie. Ingredients and concentrations of the synthetic raw water can be found in Table 1 and a characterization of the Lake Erie water can be found in Table 2.

Table 1: Wastewater ingredients and concentrations

Ingredients	Synthetic Raw Water
Peptone	2.703
Humic Acid	4.246
Sodium Lauryle Sulfate	0.942
Tannic Acid	4.175
$CaCl_2$	7350
NaCl	3000

Table 2: Characteristics of Lake Erie, Average of 8 samples

Characteristic	Measurement
Turbidity (NTU)	1.995
UV-254 (1/cm)	0.063
TDS (ppm)	235.4
Conductivity (S/cm)	353.8
pH	7.98
Hardness (mg/L as $CaCO_3$)	224.7
DOC (ppm)	4.61

The presence of microorganisms was not only necessary to mimic actual water, but also to allow for bacteria based analysis. Inoculating the water with *Pseudomonas fluorescens* and *Spirillium volutans* made it possible to perform biofouling tests. The first organism, *Pseudomonas fluorescens* strain P17, belongs to the kingdom *Monera*, the family *Pseudomonadaceae*, and the genus *Pseudomonas*. P17 forms 3 mm round, smooth, yellow colonies with straight or slightly curved rod cells ranging in size from

0.5-1.0 x 1.5-5.0 m. It is an aerobic gram-negative, catalase positive, oxidase positive, and not capable of storing poly-β-hydroxybutyrate, a polyester form of carbon. The optimum growth rate range for P17 is 25-30°C.

The second organism added to the raw water, *Spirillium volutans* strain NOX, belongs to the kingdom *Procaryote*, the family *Spirillum*, and the genus *Spirillum*. These colonies are 1 mm round, smooth, drop-like, and are either transparent or white. The bacterial cells are rigid helical, 1.4-4.7 m in diameter and 14-60 m in length, and contain large bipolar tufts of flagella. These two bacteria were selected because of the substances each metabolizes. P17 has the ability to degrade a variety of compounds, including amino acids, carboxylic acids, hydrocarboxylic acids, and carbohydrates, but it does not utilize oxalic acid (Huck, 1990). On the other hand, NOX utilizes carboxylic acids but not carbohydrates, alcohols, aromatic acids, or amino acids (van der Kooij, 1990). The wastewater was inoculated with a concentration of $1x10^3$ cfu/mL of each bacterium. After the baseline testing was completed only water collected from Lake Erie was used as a raw water.

Reagents, Glassware, Water, and Materials for Analyses

Glassware (flasks, vials, solution bottles, etc.) was cleaned in a laboratory sink following a treatment, which involved detergent wash, acid wash, and a minimum of three DI water rinses. Following this cleaning, the mouth of the glassware was covered with aluminum foil and muffled at 550 C in a laboratory oven for a minimum of four hours. This was done to remove any organic contamination. After muffling, the glassware remained covered with foil until it was used.

Silicon/PTFE septa, vial caps, and bottle caps were pretreated by covering and heating them in a 100 mg/L sodium persulfate solution for 30 minutes. The heat was controlled, so that the sodium persulfate did not boil. The treated septa and caps were stored in a cleaned and covered beaker until used.

The DI water used for cleaning glassware, making solutions, etc. met or exceeded Type I reagent water specifications provided in Table 1080:I of Standard Method (APHA, 1995). Purified water for microbiological testing met the quality criteria specified in Table 9020:I of Standard Methods (APHA, 1995).

Below is a list of the reagents, along with their ingredients, made and used for this study:

21% Acid Reagent for TOC analyzer: 37 mL of 85% Phosphoric Acid added to 188 mL DI water.

10% Persulfate & 5% Phosphoric Acid Reagent for TOC analyzer: 25 g of $Na_2S_2O_8$ and 9 mL of 85% Phosphoric Acid added to 213 mL of DI water.

2000 ppm C standard: 425 mg of KHP ($C_8H_5O_4K$) added to 100 mL of DI water.

200 ppm C standard: 10 mL of 2000 ppm C added to 100 mL of DI.

10, 5, 1 ppm C standards for calibration of TOC analyzer: 50, 25, 5 mL, respectively, of 200 ppm C into volumetric flask; filled flask with DI water unit it reached the 1-liter mark.

Mineral Salts Buffer Stock Solution: 7.0 g K_2HPO_4, 3.0 g KH_2PO_4, 0.1 g $MgSO_4*7H_2O$, 1.0 g $(NH_4)_2SO_4$, 0.1 g NaCl, 1.8 mg $FeSO_4*7H_2O$, 1.0 L DI water; this solution was autoclaved before use.

Mineral Salts Buffer Working Solution (MSB): Used a cleaned volumetric pipette with sterile tip to add 1 mL Mineral Salts Buffer Stock Solution to 999 mL DI water in a volumetric flask; this solution was autoclaved before use.

Stock Sodium Acetate Solution (200 mg/L): In a cleaned volumetric flask, DI water was added to 1.134 g of $NaCH_3COOH*3H_2O$ until volume was 1 L; this solution was autoclaved before use.

2 mg/L Sodium Acetate for BDOC test control: Added 1 mL Mineral Salts Buffer Stock Solution to 10 mL Stock Sodium Acetate Solution. Filled with DI water to the 1-liter mark; this solution was autoclaved before use.

Sodium Thiosulfate solution 10% (w/V) for chlorine neutralization: 100 g of $Na_2S_2O_3$ was dissolved in 1 liter of DI water; this solution was autoclaved before use.

Sodium Persulfate solution for treating caps and septa: 100 mg of sodium persulfate was placed into a 1-liter volumetric flask and filled to the 1-liter mark with DI water.

Acid Wash for glassware cleaning: Added 4.25 mL of Hydrochloric Acid to 250 mL DI water.

Filtration Test Apparatus and Procedures

Testing was conducted using the filtration assembly shown in Figure 1. The membrane was housed in a SEPA CF filtration unit (Osmontics, Minneatonka, MN). The filtration unit was constructed out of 316 stainless steel and rated for an operating pressure up to 69 bar (1000 psi). The test unit was sealed by applying adequate pressure via the hand pump (P-142, Enerpac, Milwaukee, WI); this ensured water was not able to bypass the membrane. The feed stream was delivered by a motor (Baldor Electric Company, Ft. Smith, AR) and M-03 Hydra-Cell pump (Wanner Engineering, Inc., Minneapolis, MN) assembly. Flow valves controlled permeate and concentrate flow and the pressure acting on the membrane in the test unit.

Due to the high pressures required by the membranes, it was necessary to use a cooling bath to control the temperature of the feed. The feed water reservoir was placed in a large bucket, which contained water and ice packs. The ice packs were continually replaced throughout the test.

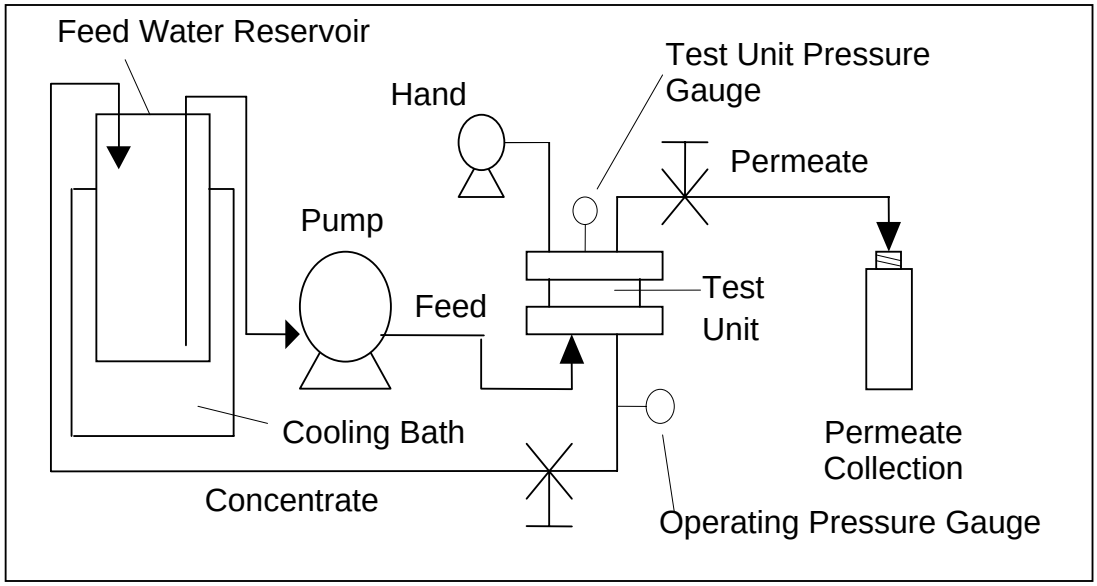

Figure 1:Filtration Assembly

This testing setup was representative of actual membrane filtration, because the test unit was operated at a pressure within each membrane's recommended operating range. Additionally, the SEPA CF is a cross-flow filtration module, which is the most common mode of operation in actual membrane filtration processes.

Before use, each membrane was rinsed with deionized (DI) water and then soaked in DI water overnight (Hong and Elimelech, 1997). The membrane was removed from the DI water and rinsed immediately before installation into the filtration cell unit. The filtration conditions (operating pressure and duration of test) depended on the physical limitations and flux of each membrane. Once the membrane was installed in the filtration cell unit, the membrane was pre-compacted with 1000 mL of DI water. (Hong and Elimelech, 1997). The soaking in DI and the pre-compactions with DI is necessary to stabilize the membrane flux and rejections (Hong and Elimelech, 1997). Initially, the pores of membranes are filled with air; soaking in and pre-compaction with DI water

helps remove the air from the pores by 'pushing' it out. Immediately following the DI water, the raw water was added to the feed container. A 500 mL sample of the raw water is taken before testing and is stored for water quality analysis. The first 2000 mL of permeate from raw water filtration was discarded to ensure complete removal of DI water from the test unit. After this disposal, permeate was collected in an organic free bottle for water quality analysis. This analysis required that 1000 mL of permeate to be collected.

Throughout the test, membrane flux was measured by recording the time required to collect 50 mL of permeate. To compensate for variations in pressure and changes in feed water temperature (changes in viscosity of the water), each flux measurement was accompanied by a measurement of the operating pressure and temperature of the feed water. This allowed for normalization of the solvent mass transfer coefficient (MTC, also known as specific flux) defined as

$$MTC_{25^\circ C} \equiv \left[\frac{J}{\Delta P}\right]_{T(^\circ C)}\left[\frac{\mu_{25^\circ C}}{\mu_{T(^\circ C)}}\right] \qquad (1)$$

where J (m/s*kPa) is flux, ΔP (kPa) is the operating pressure, and is viscosity (N·s/m^2).

After collection of permeate for water quality analysis, the membrane/film assembly was removed from the SEPA CF test unit and went through water quality analysis. A 500 mL sample of the remaining raw water, further known as concentrate, was also kept for water quality analysis.

Water Quality Analysis

The water quality of the feed water, permeate, and concentrate was determined by TDS, pH, turbidity, conductivity, hardness, DOC, UV-254, and HPC analysis. A brief description and method identification for each analysis follows.

Conductivity was measured by a Traceable Digital Conductivity Meter (Control Company, Friendswood, TX).

Total dissolved solids are related to conductivity and were also measured by the Traceable Digital Conductivity Meter (Control Company, Friendswood, TX).

pH was measured according to Standard Method #4500-H^+ B (APHA, 1995). The instrument used was the pH meter 430 (Corning Inc., New York).

Turbidity measurements were performed according to Standard Method #2130B (APHA, 1995). The instrument used was the MICRO 100 Turbidimeter (HF Scientific, Ft. Meyers, FL).

DOC analysis was performed using a Phoenix 8000 TOC analyzer (Tekmar-Dohrmann, Cincinnati, OH). Before analysis, the samples were filtered through a 0.45 m pore size nylon filter (Whatman International Ltd., Maidstone, England) to remove any solids; this was necessary to prevent damage to the instrument.

UV-254 served as a measurement of low concentrations of saturated organic compounds such as benzene-ring-containing compounds or unsaturated straight-chain compounds containing double bonds. The instrument used was the Genesys 8 UV/Visible Spectrophotometer (Spectronic Unicam, Rochester, NY).

Heterotrophic plate counts (HPC) were done utilizing the spread plate method outlined in Standard Method #9215 C (APHA, 1995).

Hardness was determined using the EDTA titration method according to Standard Method #2340C (APHA, 1995).

Membrane Fouling Analysis

The severity of abiotic fouling was determined by assessing the NOM accumulation on the membrane surface. This was accomplished through a membrane autopsy after filtration experimentation had been completed. The membrane autopsy was performed according to the method proposed by Hong and Elimelech (1997). A sample portion from the used membrane and an unused control were placed into separate 100 mL 0.1 M NaOH solutions overnight to dissolve the NOM. After complete removal of the NOM from the membrane surface, the resulting solutions were analyzed for turbidity, conductivity, TDS, and UV-254. The samples used for UV-254 analysis were first filtered through a 0.45 m pore size nylon filter (Whatman International Ltd., Maidstone, England); this ensured solids did not interfere with the analysis. To account for contributions in the readings from the 0.1 M NaOH solution, a clean, unused membrane sample was subjected to the same conditions and testing as the used membrane. The difference in the results of each analysis (unused membrane result subtracted from used membrane result) was considered the amount of abiotic fouling on the used membrane. The mass of the foulants on the membrane was determined using the method developed in Hong and Elimelech (1997).

Biofouling was measured by aseptically transferring the membrane into a stomacher bag with 100 mL of mineral salts buffer working solution. The bag was sealed and placed into a Stomacher 400 Circulator (Seward, London, England), which was

operated at normal speed (230 RPM) for two minutes. A detailed description of the stomacher removal technique by Ollos (1998) was followed. Bacterial accumulation on the membrane surface was then measured according to Standard Method #9215C (APHA, 1995).

Determining Coagulant and Dosage

A standard jar testing procedure was used to determine the most effective coagulant and optimum dosage. Water collected from Lake Erie was used as the raw water. Solutions of 2% (20,000 mg/L) of ferric chloride and ferrous chloride were tested. A 1000 mL square beaker was filled with raw water and stirred at the maximum speed of 300 rpm. At time equal to 0 seconds the coagulant was added into the vortex around the shaft of the mixer to ensure better and instantaneous mixing and was mixed at 300 rpm for 2 minutes. At time equal to 120 seconds the mixing was reduced to 200 rpm for 45 seconds. At this time the mixing was stopped and the floc was allowed to settle for 2 minutes, at which time a 100 mL sample was taken. The water quality of each sample was determined by TDS, pH, turbidity, conductivity, and UV-254 analysis. Brief descriptions and method identifications can be found above. The dosage of coagulant was determined by using equation 3 below.

$$\frac{\text{Desired Dosage (mg/L)} \times \text{Volume of Jar (mL)}}{\text{Solution Concentration (mg/L)}} \equiv \text{Dose of Coagulant (mL)} \qquad (3)$$

For initial testing, doses of 0, 25, 50, 75, and 100 mg/L of coagulant were used. Further testing of ferric chloride was done using doses of 0, 5, 10, 15, 20, and 25 mg/L.

Coagulation Setups

Four methods of coagulant pretreatment were tested, a conventional coagulant/settlement, two dynamic membrane, and an inline setup.

Conventional Coagulant/Settlement

For this setup, 4 L of raw water, collected from Lake Erie, were used along with the CQ and NTR membranes. A 2000 mL valved outlet reservoir bottle was filled with raw water and was stirred using a magnetic stirrer at the maximum setting of ten. At time equal to 0 seconds, 5 mL of 2% ferric chloride were added into the vortex created by the mixer to ensure better and instantaneous mixing and mixing followed for 2 minutes. At time equal to 120 seconds, the mixing was reduced to a setting of five for 45 seconds. At this time, the mixing was stopped and the floc was allowed to settle for 20 minutes. This procedure was repeated and after the floc was allowed to settle, the water was drained using the valve into one 4 L bottle. This was used as the raw water in the filtration process described previously.

Dynamic Membrane

Two different setups were used to test this method of coagulation the pretreatment, both setups tested the CQ membrane with water collected from Lake Erie. One test was run with NTR and Lake Erie raw water, but due to the properties of the membrane, a severe flux decline was observed and it was decided that no improvement could be made to the membrane with this pretreatment. The first setup utilized the membrane filtration method above, but after the membrane had been pre-compacted with

1000 mL of DI water, a solution of 10 g ferric chloride/10 mL DI water were placed on the plastic film that is in direct contact with the membrane surface. To allow binding to the membrane and rinsing of excess coagulant another 1000 mL of DI water was run across the membrane before filtering the raw water. After the 1000 mL of permeate had been collected, another bottle of raw water was filtered. The first 2000 mL of permeate were again discarded and after this disposal, permeate was collected in an organic free bottle for water quality analysis.

For the second dynamic membrane setup, a solution of 10g ferric chloride/1000 mL DI water was filtered in a dead-end mode (0% recovery) across the membrane using the pump after the membrane had been pre-compacted with 1000 mL of DI water. An additional 1000 mL of DI water was filtered to allow the excess coagulant to be rinsed away. Two bottles of raw water were filtered with the first 2000 mL of permeate being discarded and the third 1000 mL of permeate being collected in an organic free bottle.

Inline Testing

This setup tested the CQ membrane with water collected from Lake Erie. The original membrane filtration method was used until the 1000 mL of permeate was to be collected. At this time the pump's inlet line was replaced with the setup shown in Figure 2. The 3/8" tube was split with a tee and off of the tee a 3/8" to ¼" reducer was coupled to valve which was then connected to ¼" tubing. This new line was used to introduce coagulant into the raw water before it crossed the membrane surface.

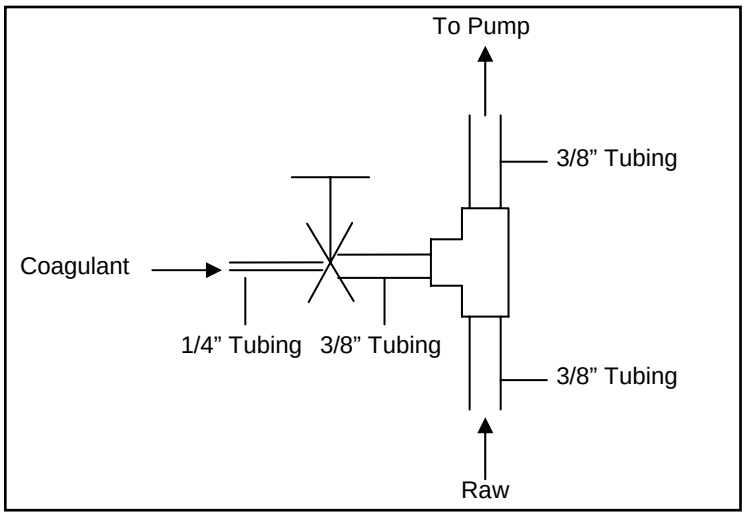

Figure 2: Inline Setup

The coagulant used for this test was 500 mL of 2% ferric chloride. After the coagulant had been run in, the extra line was placed in the raw water, so that air was not sucked into the inlet line. Again the 1000 mL of permeate was collected in the organic free bottle. The same water quality testing was done on the samples as was done previously.

RESULTS

Task 1 – Characterize different membranes using bench scale filtration experiments

The objective of this task was to establish baseline data for two purposes. The first purpose was to choose the worst performers with respect to flux decline and rejection efficiency. The worst performer is the one targeted for improvement through coagulant pretreatment. The second purpose of the baseline, specifically the Lake Erie baseline, is for comparison with later testing. In Figures 3 and 4, the MTC data for each run is shown. Figure 3 shows the data for the laboratory designed raw water, while Figure 4 shows the data for the Lake Erie water. It is observed in these figures that although ESPA and CK have low MTC values they do not show a flux decline. In these figures, especially Figure 4, CQ shows a lot of variability.

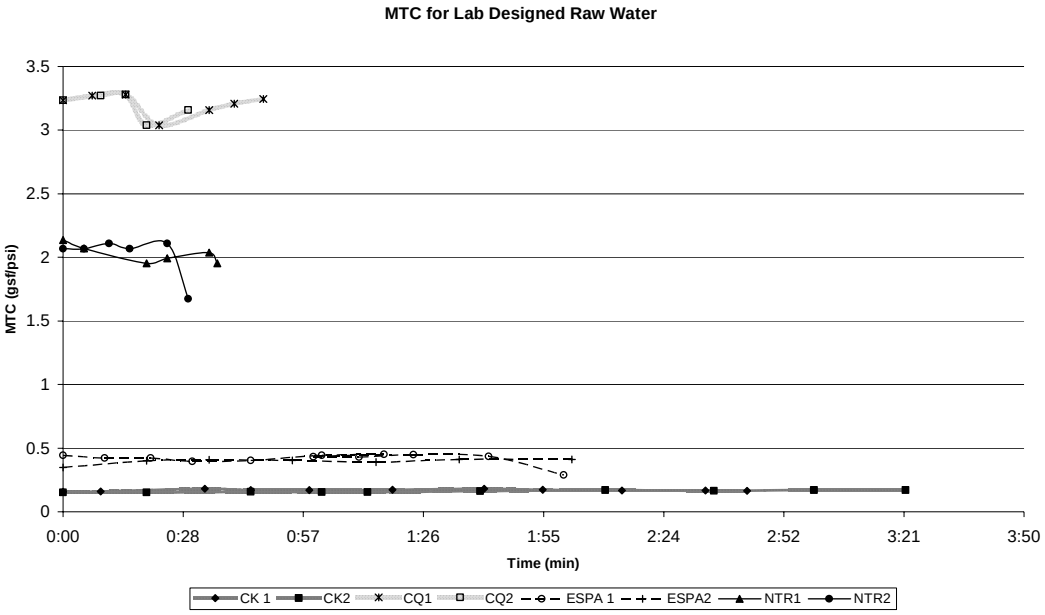

Figure 3: MTC for Laboratory Designed Raw Water

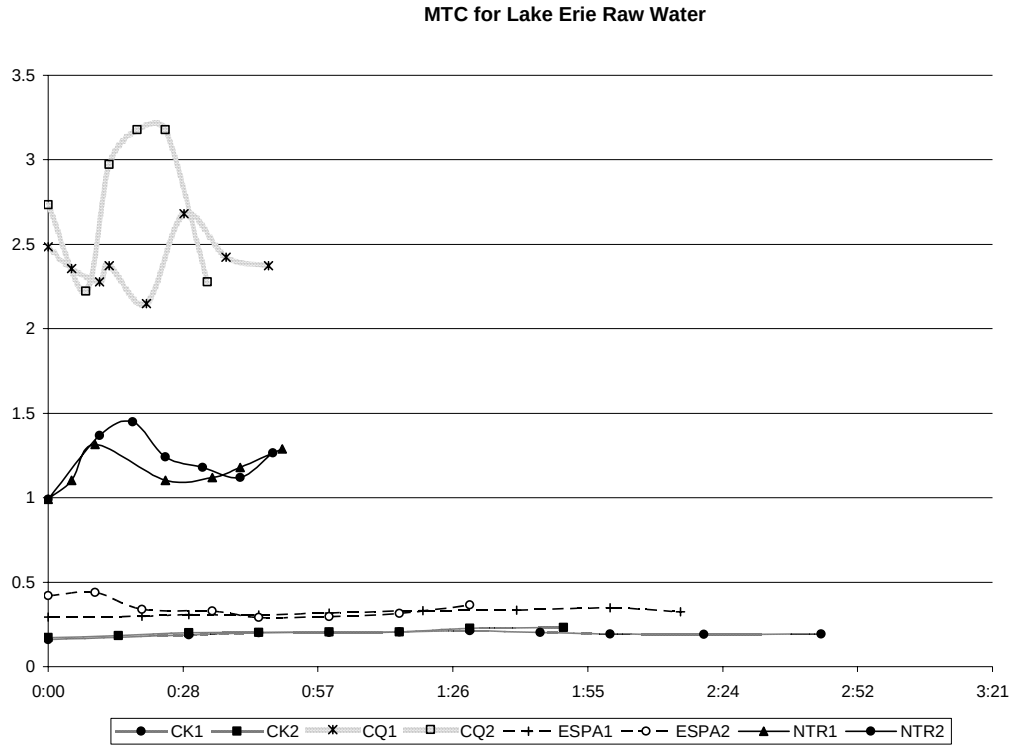

Figure 4: MTC for Lake Erie Raw Water

The water quality data for Task 1 can be seen in Tables 3 and 4, laboratory designed and Lake Erie waters, respectively. From Table 3, the percent removals of UV254, TDS, conductivity and hardness for the CQ and NTR membranes were the lowest. In agreement with Table 3, Table 4 shows that CQ and NTR had a lower performance than ESPA and CK. Thus, due to CQ's performance during baseline testing, it was chosen to run with the coagulant to determine if flux could be improved and stabilized, and if permeate quality could be improved.

Table 3: Baseline water quality results for lab designed raw water.

Summary of Reduction Percentages Between Lab Designed Raw Water and Permeate				
	CK	**CQ**	**ESPA**	**NTR**
Turbidity (NTU)	98.98%	97.02%	86.72%	87.91%
UV254	70.43%	41.60%	77.87%	-27.01%
TDS (ppm)	61.68%	6.96%	86.27%	5.96%
Conductivity (uS/cm)	61.57%	6.98%	88.90%	6.36%
PH	-3.49%	1.25%	-15.29%	-4.40%
Hardness	90.14%	9.22%	55.65%	17.62%
Bacteria Reduction	99.13%	96.26%	93.76%	98.48%
n=2 for all membranes tested				

Table 4: Baseline water quality results for Lake Erie raw water.

Summary of Reduction Percentages Between Raw Water and Permeate				
	CK	**CQ**	**ESPA**	**NTR**
Turbidity (NTU)	98.89%	98.76%	63.70%	22.37%
UV254	-44.76%	32.72%	21.01%	61.64%
TDS (ppm)	72.58%	4.94%	74.77%	6.03%
Conductivity (uS/cm)	72.78%	4.92%	75.01%	6.20%
PH	7.55%	0.93%	2.24%	-0.69%
Hardness	20.83%	25.76%	76.67%	6.67%
Bacteria Reduction	98.02%	49.82%	97.35%	95.45%
n=2 for all membranes tested				

Task 2 – Optimal coagulant type/dose determination

The objective of Task 2 was to determine which coagulant and dosage would be the most effective in treating water collected from Lake Erie. Tables 5 and 6 show the results from the first round of testing, which was used to determine if ferric or ferrous chloride would be a more effective coagulant. It was determined that ferric chloride in the range of 0 to 25 mg/L showed the greatest improvement, therefore was tested in smaller increments. Table 7 shows the results of the second round of testing, from which, the results were observed to be similar for each of the properties tested except for UV254. With respect to UV254, it was determined that ferric chloride at a dosage of 25 mg/L was the most effective, and thus was chosen as the coagulant to be used in Task 3.

Table 5: Water Quality Results for Ferrous Chloride

Coagulant Testing for 2% Ferrous Chloride					
	Turbidity	**pH**	**TDS**	**Conductivity**	**UV-254**
Control	4.305	7.770	268.5	403.0	0.106
0 mg/L	2.235	7.580	286.5	431.0	0.066
25 mg/L	34.650	7.445	289.5	434.0	0.027
50 mg/L	81.000	7.215	295.0	444.0	0.037
75 mg/L	131.000	7.220	302.5	454.0	0.056
100 mg/L	231.000	7.355	309.5	463.5	0.066

Table 6: Water Quality Results for Ferric Chloride

Coagulant Testing for 2% Ferric Chloride					
	Turbidity	**pH**	**TDS**	**Conductivity**	**UV-254**
Control	4.305	7.770	268.5	403.0	0.106
0 mg/L	1.880	7.425	271.0	406.5	0.101
25 mg/L	8.050	7.285	277.5	416.5	0.050
50 mg/L	14.450	7.125	284.0	426.5	0.045
75 mg/L	20.150	6.995	289.0	435.0	0.042
100 mg/L	20.600	6.815	300.0	450.5	0.039

Table 7: Water Quality Results for Second Round of Testing of Ferric Chloride

Coagulant Testing for 2% Ferric Chloride					
	Turbidity	**pH**	**TDS**	**Conductivity**	**UV-254**
Control	3.615	7.665	283.5	425.0	0.075
0 mg/L	2.535	7.515	292.0	436.0	0.050
5 mg/L	4.015	7.245	291.0	437.5	0.130
10 mg/L	5.160	7.180	289.5	435.0	0.121
15 mg/L	6.475	7.095	289.0	434.0	0.096
20 mg/L	7.325	7.070	291.5	437.0	0.091
25 mg/L	6.760	7.055	291.0	437.0	0.044

Task 3 – Pretreatment comparison

The MTC results for each of the tests are shown in Figures 5-8 and the water quality results are shown in Tables 8-11. Each figure shows the data collected during baseline testing and the data collected during each coagulant set up. Trend lines were added to indicate how each MTC was affected by the test. The tables summarize percent removals for key water quality characteristics.

Conventional Coagulation

Figure 5 shows the MTC values for baseline testing and the conventional coagulation. It is seen that the baseline testing shows great variability. For conventional coagulation, a larger MTC decline was observed with no regain. This was likely due to the presence of suspended flocs in the feed water that could foul the membrane. Table 8 shows a comparison between the removal percentages of TDS, hardness and DOC. The average feed water TDS values were 515 and 240 ppm for baseline and conventional coagulation, respectively, while for the permeate, TDS values were 480 and 240 ppm, respectively. Table 8 shows that the rejection of dissolved solids (TDS) is almost negligible for both the baseline and conventional coagulation tests, which was expected due to the large pore size of UF membranes, such as CQ. For hardness, the average feed water values were 123 and 213 mg/L as $CaCO_3$ baseline and conventional coagulation, respectively, while for the permeate, hardness values were 111 and 192 mg/L as $CaCO_3$, respectively. Both tests showed similar rejection efficiencies for hardness. Regarding DOC, the average feed water values were 0.91 and 5.22 mg/L baseline and conventional coagulation, respectively, while for the permeate, hardness values were 1.01 and 3.40 mg/L, respectively. Conventional coagulation shows a higher rejection of DOC than the baseline, which indicates that coagulation was effective in removing organic carbon from the raw water. Looking at these results it was determined that conventional coagulation was not ideal for Lake Erie water.

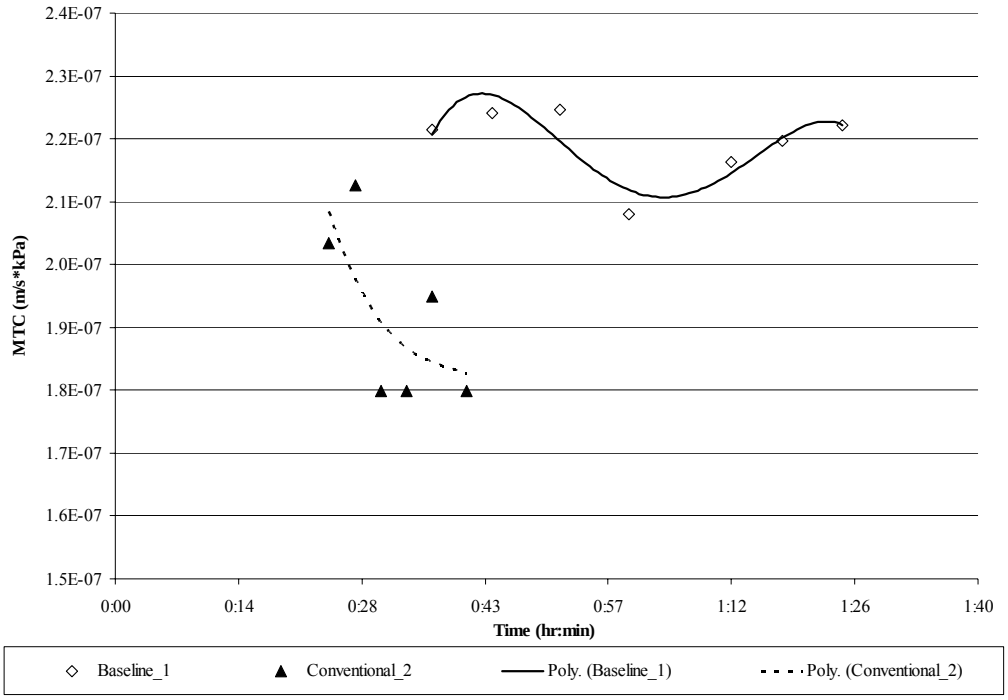

Figure 5: Comparison of MTC Values of baseline testing versus conventional coagulation.

Table 8: Comparison of percent removals between baseline and conventional coagulation.

	Baseline	**Conventional**
TDS (mg/L)	6.9%	0.0%
Hardness (mg/L as $CaCO_3$)	9.4%	9.9%
DOC (mg/L)	0.0%	34.9%

Slurry

Fig. 4 shows a comparison of the baseline data to the slurry data. Again, the data points are shown for each test and then trend lines are added to characterize the MTC behavior. It was observed for the slurry tests that the MTC had a greater initial value and although there was a greater decline, the ending trend was in a positive direction.

Initially, the coagulant slurry blocks the support pores, which led to a flux decline. Once the pores are blocked, a transition time is said to have elapsed and the formation of a steady-state filtration layer begins, during which the flux is regained. Table 9 shows a comparison between the removal percentages of TDS, hardness and DOC for the two tests. The average feed water TDS values were 515 and 222 ppm for baseline and conventional coagulation, respectively, while for the permeate, TDS values were 480 and 210 ppm, respectively. Table 9 shows that the rejection of TDS is almost negligible for both the baseline and slurry tests. For hardness, the average feed water values were 123 and 236 mg/L as $CaCO_3$ baseline and conventional coagulation, respectively, while for the permeate, hardness values were 111 and 201 mg/L as $CaCO_3$, respectively. The slurry showed higher rejection efficiencies for hardness. Regarding DOC, the average feed water values were 0.91 and 4.14 mg/L baseline and conventional coagulation, respectively, while for the permeate, hardness values were 1.01 and 2.75 mg/L, respectively. Slurry shows a higher rejection of DOC than the baseline. Due to slurry's improvement of MTC and water quality, it is the most effective pre-treatment method for Lake Erie water.

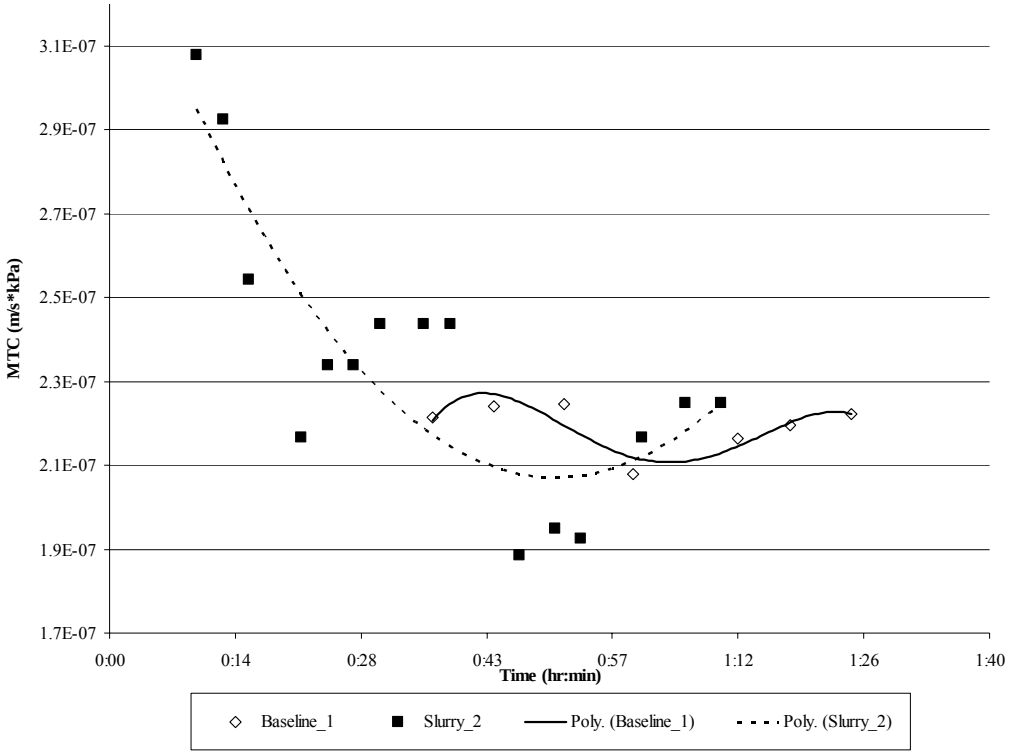

Figure 6: Comparison of MTC values for baseline testing versus slurry testing.

Table 9: Comparison of percent removals between baseline and slurry testing.

	Baseline	**Slurry**
TDS (mg/L)	6.9%	5.2%
Hardness (mg/L as $CaCO_3$)	9.4%	14.6%
DOC (mg/L)	0.0%	33.7%

Dynamic Membrane

Fig. 5 shows a comparison of the baseline data to the dynamic membrane data. Due to its similarity to the slurry testing the results are comparable to the slurry results.

There is an initial increase in MTC, then a greater decline, and then an upward trend towards the end of the test as the dynamic membrane initially blocks pores and after some time forms a steady-state coagulant layer on the membrane surface. Table 10 shows a comparison between the removal percentages of TDS, hardness and DOC for baseline and dynamic membrane testing. The average feed water TDS values were 515 and 222 ppm for baseline and conventional coagulation, respectively, while for the permeate, TDS values were 480 and 196 ppm, respectively. Table 10 shows that the dynamic membrane showed a lower percent removal of TDS than the baseline testing. For hardness, the average feed water values were 123 and 230 mg/L as $CaCO_3$ baseline and conventional coagulation, respectively, while for the permeate, hardness values were 111 and 203 mg/L as $CaCO_3$, respectively. The dynamic membrane showed a slight improvement in the rejection efficiency for hardness. Regarding DOC, the average feed water values were 0.91 and 1.89 mg/L baseline and conventional coagulation, respectively, while for the permeate, hardness values were 1.01 and 2.75 mg/L, respectively. As with hardness, there was a slight improvement in the rejection of DOC by the dynamic membrane test.

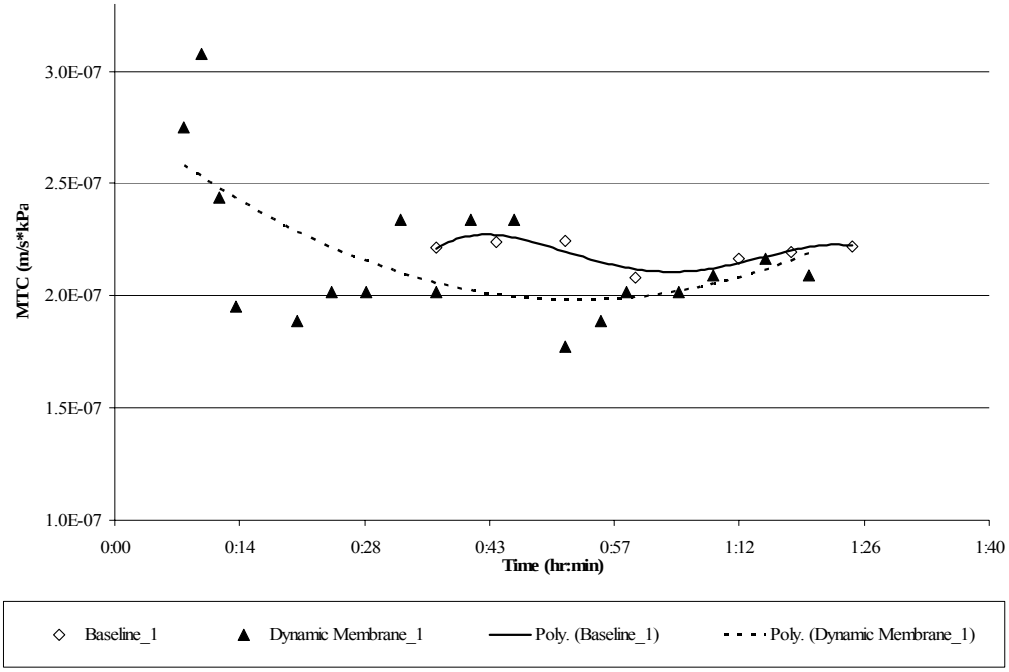

Figure 7: Comparison of MTC values for baseline versus dynamic membrane.

Table 10: Comparison of percent removals between baseline and dynamic membrane.

	Baseline	**Dynamic Membrane**
TDS (mg/L)	6.9%	3.2%
Hardness (mg/L as $CaCO_3$)	9.4%	11.7%
DOC (mg/L)	0.0%	12.1%

Inline Coagulation

Fig. 6 shows a comparison of the baseline to the inline coagulation data. The results show, that overall the MTC values are lower and that the inline coagulation causes a greater decrease in MTC. This decline most likely occurred because the coagulant attached to the particles that had already fouled the membrane, thereby increasing the cake layer and causing a further decline in the MTC. Table 11 shows a comparison between the removal percentages of TDS, hardness and DOC for the two tests. Looking at the table it is seen that the inline testing does not improve water quality. The average feed water TDS values were 515 and 236 ppm for baseline and conventional coagulation, respectively, while for the permeate, TDS values were 480 and 196 ppm, respectively. Table 11 shows that the inline coagulation showed no removal of TDS. The MTC and water quality results indicate that inline testing is not a good option for Lake Erie water.

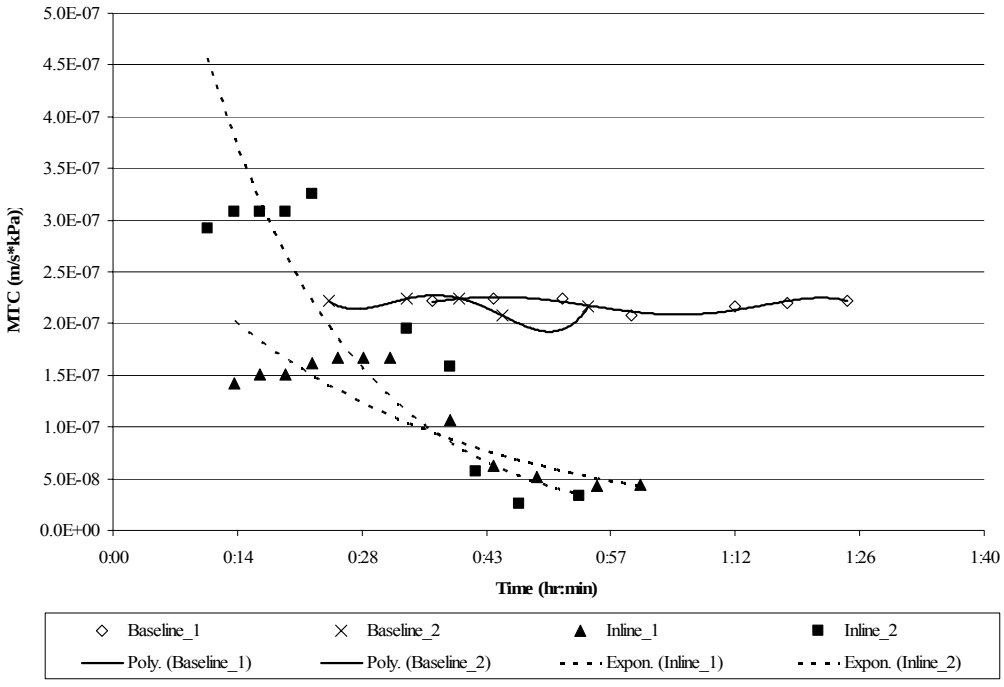

Figure 8: Comparison of MTC values for baseline versus in-line coagulation.

Table 11: Comparison of percent removals between baseline and inline coagulation.

	Baseline	**Inline**
TDS (mg/L)	6.9%	0.0%
Hardness (mg/L as $CaCO_3$)	9.4%	N/A
DOC (mg/L)	0.0%	N/A

DISCUSSION

Figure 9 shows an overall comparison of specific flux decline for the baseline and for all pretreatment alternatives tested. Despite their higher initial flux values and higher initial flux decline, both the slurry and dynamic membrane operations show steady-state flux values similar to those of the baseline. As previously stated, these observations were due to the initial blocking of pores by the coagulants and, after some time, the formation of a steady-state layer on the membrane. On the other hand, conventional coagulation and inline coagulation show lower initial flux values and significantly lower steady-state fluxes than the baseline. In Figures 10 through 14, comparisons are provided for TDS, hardness, DOC, turbidity and UV-254, and average values for the raw water are shown using the black bar and permeate values are shown using grey bars, and due to the difference in raw water characteristics, the percent removal is also shown. Overall, as previously described individually, the slurry and the dynamic membrane tests showed the best removal efficiencies. Thus, these two are the most applicable for pretreatment of Lake Erie water.

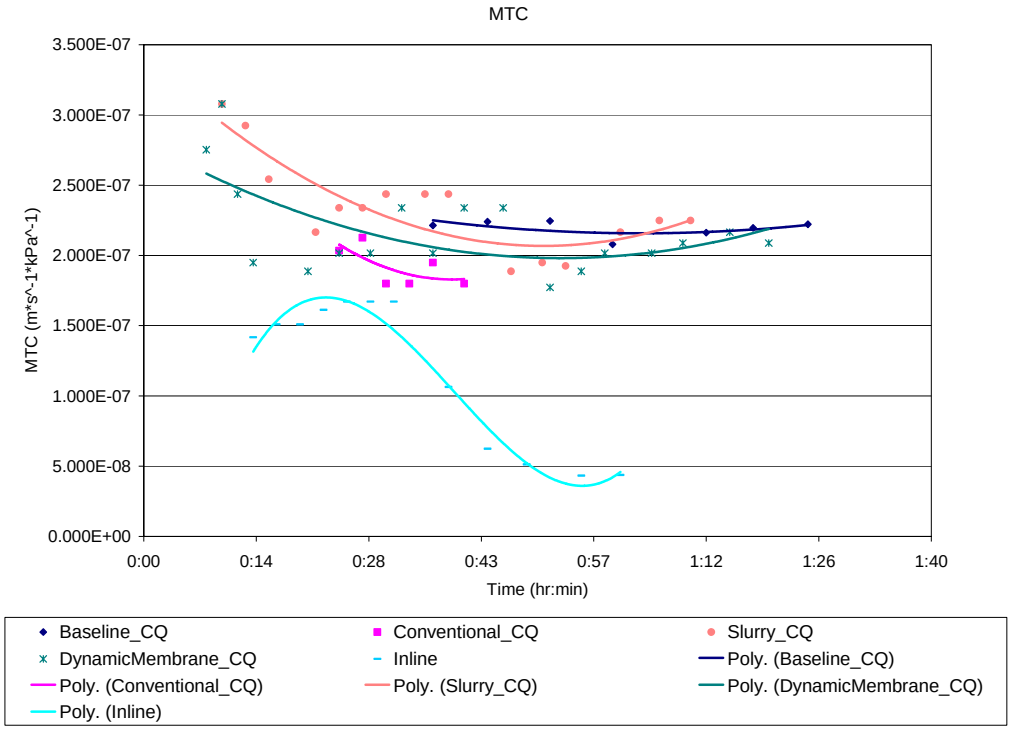

Figure 9: Overall specific flux comparison.

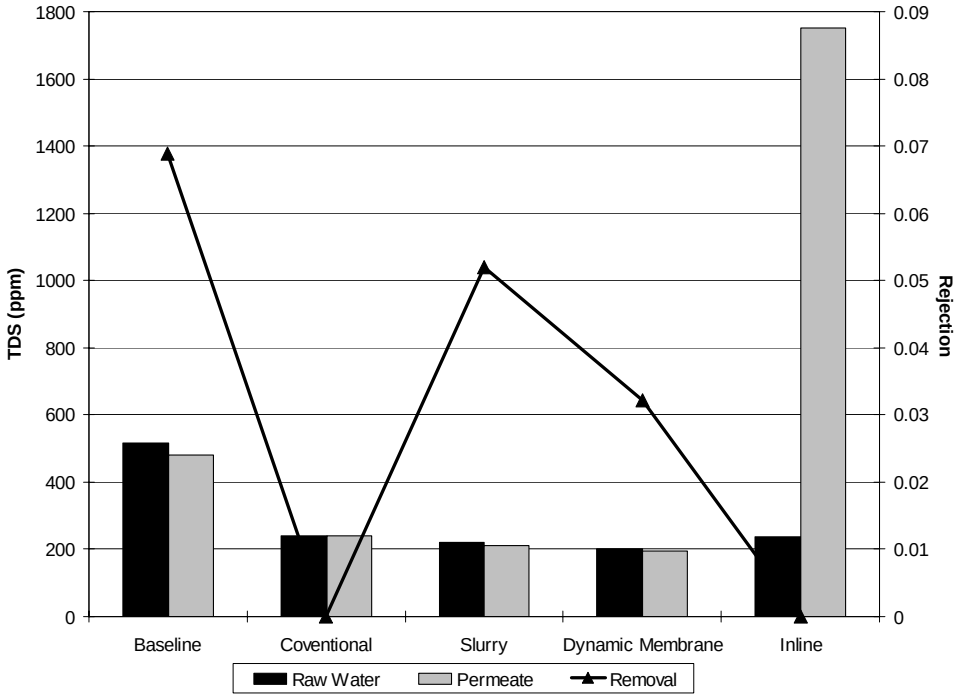

Figure 10: Comparison of TDS values between each test.

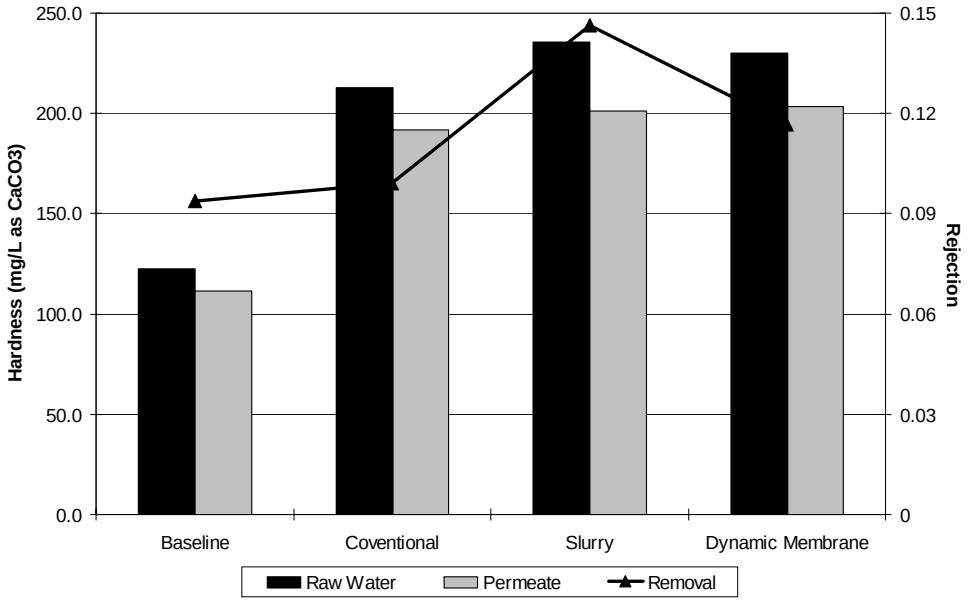

Figure 11: Comparison of hardness values between each test.

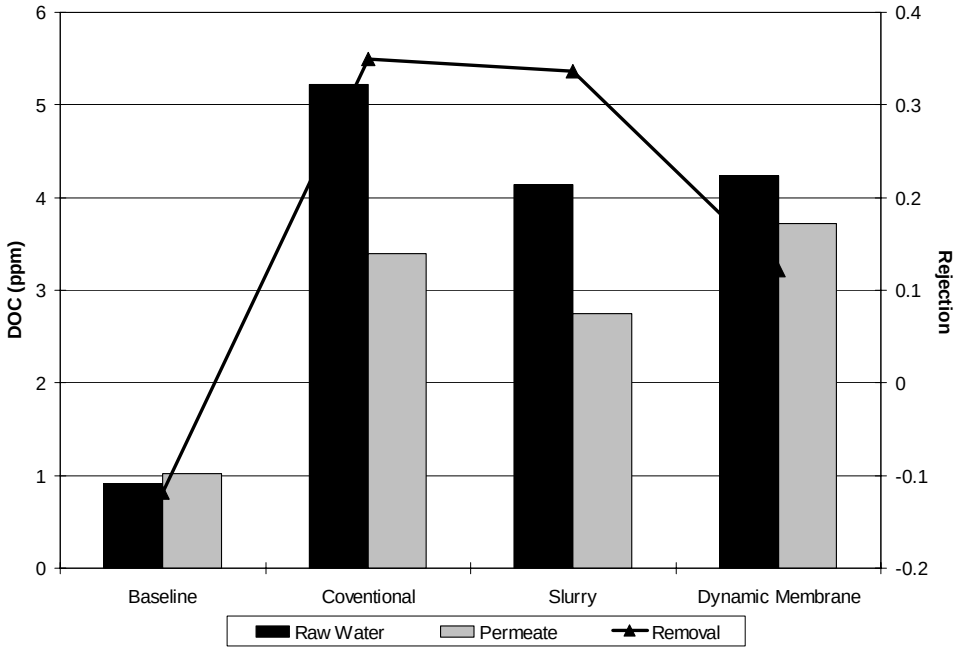

Figure 12: Comparison of DOC values between each test.

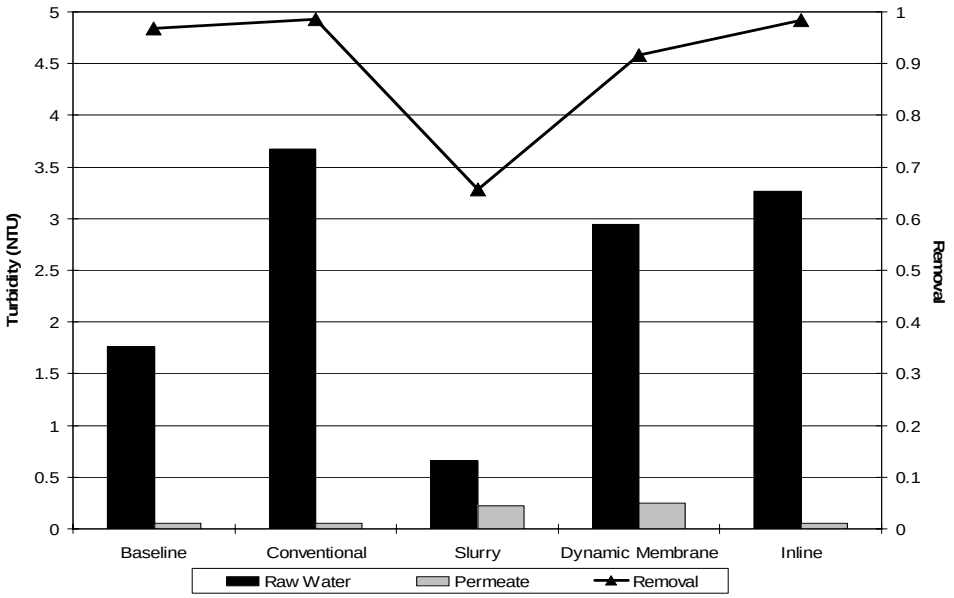

Figure 13: Comparison of turbidity values between each test.

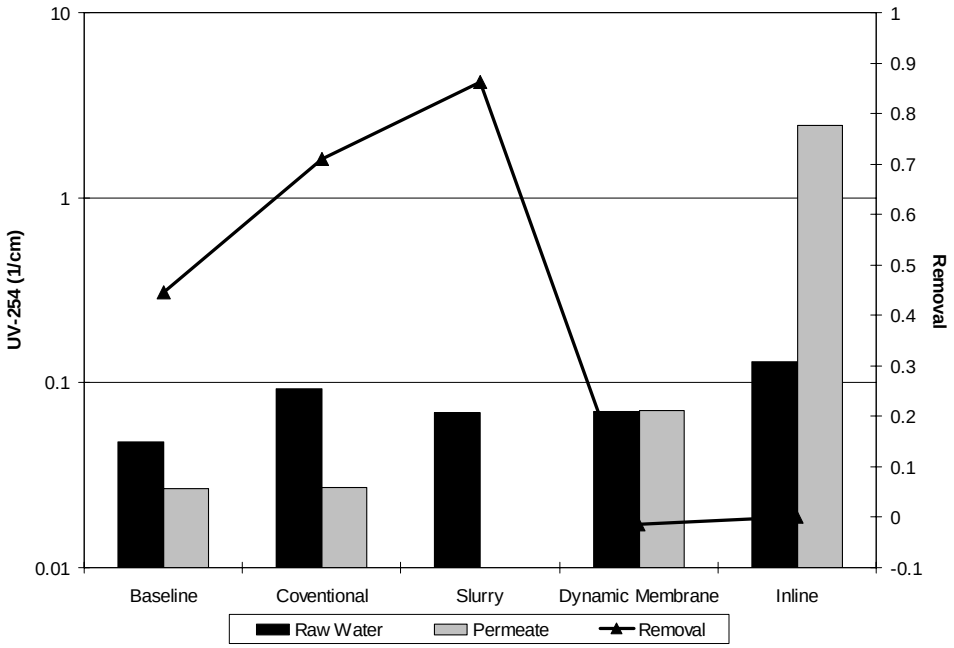

Figure 14: Comparison of UV-254 values between each test

Fouling Analysis

Figures 15 and 16 are analyses of the UV-254 and solids that were built up on the membrane. Figure 15 indicates that the conventional coagulation has the highest accumulation of UV-254 attached to the membrane, while the slurry test had the lowest. Similar results are observed in Figure 16, which shows the weights of the solids that remained on the membrane. Again conventional coagulation had the highest amount of fouling and the slurry had a very low amount of fouling.

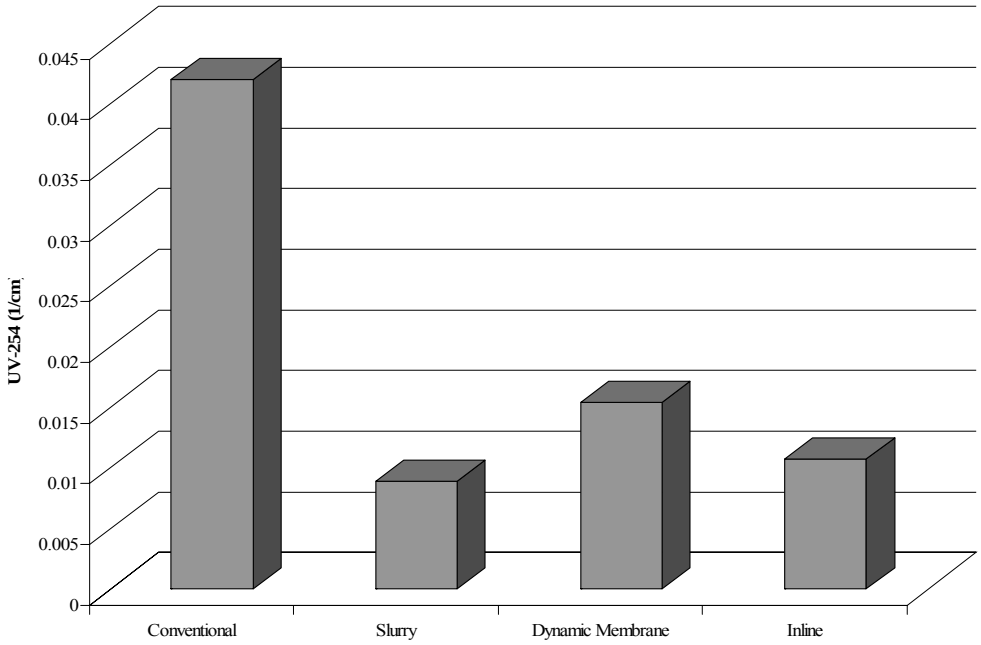

Figure 16: Comparison of UV-254 values for membrane fouling.

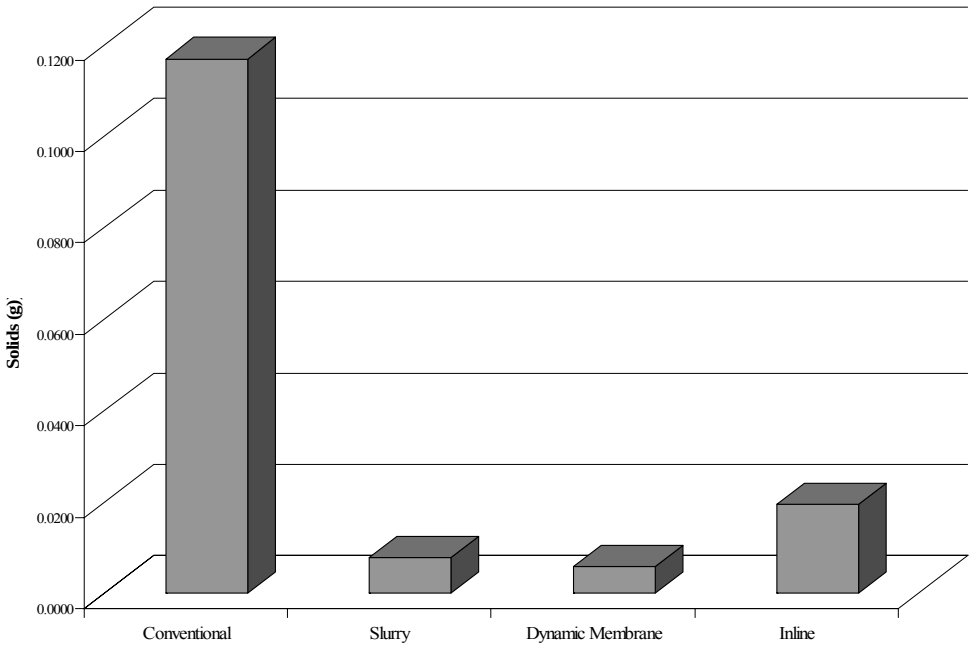

Figure 96: Comparison of solids values for membrane fouling.

From the overall comparison of all of the pretreatment options' results to those of the baseline testing, it becomes apparent that the slurry pretreatment method is the most effective for Lake Erie water. The results also show that the dynamic membrane also offers effective results. It was determined that conventional and inline coagulation could not offer improvement for Lake Erie water.

SUMMARY

- MTC
  - Conventional Coagulation
    - Similar, but overall lower
  - Slurry
    - Initial decrease, but ended with an upward trend
  - Dynamic Membrane
    - Initial decrease, but ended with an upward trend
  - Inline
    - Greater decrease in MTC
- Inorganics
  - Turbidity
    - All above 90% removal, except for slurry
  - TDS/Conductivity
    - Low removal as expected for membrane
  - Hardness
    - Removals between 9%-15% with slurry having highest removal
- Organics
  - UV254
    - Slurry had 90% removal
    - Dynamic membrane and inline did not see removal
  - DOC
    - Conventional coagulation has highest removal
    - Baseline had no removal
- Fouling
  - UV 254
    - Slurry provided the lowest value
  - Solids
    - Dynamic membrane provided the lowest value
- Overall
  - Slurry provides the best improvement
  - Dynamic membrane also provides improvement
  - Conventional and Inline coagulation are not good pretreatment methods for Lake Erie water

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